Complexes of Binucleating Ligands.
XIX. Facile Hydration of Nitriles at a Di-palladium(II) Site under Mild Conditions

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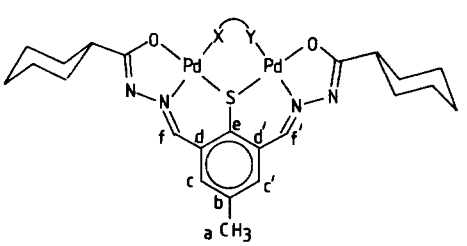
Abstract

The acetate-bridged complex $LPd_2(CH_3CO_2)$, in which L^{3-} is a previously reported binucleating ligand, reacts with hydroxide ion to generate hydroxo-LPd_2 which, molecular weight measurements suggest, exists as $[LPd_2(OH)]_{3-4}$ in chloroform solution. Hydroxo-LPd_2 reacts with nitriles at room temperature to yield the complex with the conjugate base of the corresponding amide bound at the di-palladium site. It is proposed that this unusually facile hydration of nitriles proceeds via a non-bridged intermediate in which the nitrile is bound to one palladium centre and thereby activated to nucleophilic attack, whilst the nucleophilic hydroxide is held in close proximity, bound to the second palladium.

Introduction

Attention has previously been drawn to the possible operation in complexes of binucleating ligands of an order/disorder-derived effect akin to the chelate effect which may have interesting manifestations in both the areas of structure and reactivity [1]. An anticipated structural manifestation is the stabilisation of unusual species bound at a compatible bimetallic site of a complex of an appropriate binucleating ligand, yielding molecular arrangements which would be unlikely or impossible in the absence of the organisation provided by the binucleating ligand. A number of examples of such unusual bridging species incorporated into binuclear systems of the type **I**, including several in which metal–carbon bonds are established, have been reported [1–4]. The binucleating component of the complex **I** is the one used in the work reported below which we shall refer to as L^{3-}, so that **I** would be represented as $LPd_2(XY)$. With regard to manifestations of the proposed effect in the area of reactivity, one of several possibilities which can be envisaged is that a potentially nucleophilic centre (Z in **II**) might be bound at one metal centre whilst a substrate molecule (e.g. X=Y in **II**, which is not necessarily diatomic and which may be π-bonded or σ-bonded to the metal) is attached to the adjacent metal, being thereby activated towards nucleophilic attack. Electronically and sterically the intermediate **II** is predisposed to the formation of a Z–Y bond as in **III**. In this case the association, binucleating ligand·M_2·Z, can be viewed as a bifunctional reagent providing both an acidic and a basic site appropriately disposed for reaction upon the substrate XY. The demonstration that the LPd_2^+ system can accommodate two separate ligands [5] supports the feasibility of the formation of the crucial non-bridged intermediate **II** and the ready incorporation of a wide range of 3-atom bridges [2–4] into LPd_2^+ provides reason for optimism that processes of the type **II** → **III** may be possible. In this report we describe the first example of such a process, which serves to illustrate the more general potential of complexes of binucleating ligands for promotion or catalysis of unusual reactions.

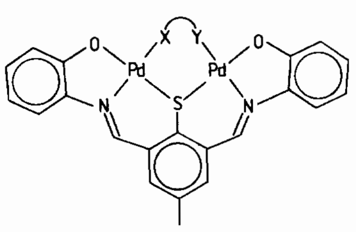


I

II **III**

Results and Discussion

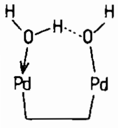
Work with a series of binuclear complexes of the type **IV**, the binucleating component of which we shall refer to as L'^{3-}, revealed that the acetate bridged complex, $L'Pd_2(CH_3CO_2)$, reacted with hydroxide ion to give an acetate- free material tentatively formulated as $L'Pd_2(OH, H_2O)$ in which the hydrogen-



IV

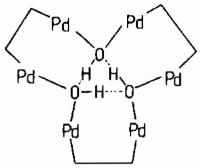
bonded bridging system shown in **V** was proposed [6]. Unfortunately, most of the $L'Pd_2^+$ derivates examined, including this hydroxo derivative, were virtually insoluble in all solvents, which very much restricted the availability of structural evidence and it was in order to circumvent these solubility problems that the binucleating ligand L^{3-} was developed.

We now report that $LPd_2(CH_3CO_2)$ also reacts readily with hydroxide ion with loss of acetate. It has proved difficult to isolate a pure product reproducibly from this reaction and, for this reason, a wide range of conditions have been explored; generally a two-phase reaction mixture was employed consisting of $LPd_2(CH_3CO_2)$ in an organic phase (either chloroform or dichloromethane or tetrahydrofuran or dioxan or benzene) and a basic aqueous phase (either hydroxide or carbonate or bicarbonate) both with and without a phase transfer agent (tetrabutylammonium cation). ^1H NMR spectra, in particular the signals arising from the imine protons H_f and $H_{f'}$ in **I** proved to be much more useful than IR spectra in monitoring these reactions. The IR spectra of isolated solids, although indicating the displacement to a major extent of the acetate group by the marked reduction in intensity of the strong acetate-derived bands at 1540 cm^{-1} (ν_{CO_2asym}) and 1420 cm^{-1} (ν_{CO_2sym}) and although displaying the detailed fingerprint features of the LPd_2^+ system expected on the basis of wide experience with a large number of LPd_2 derivatives, failed to reveal significant contamination by $LPd_2(CH_3CO_2)$ in some preparations which was clearly indicated by the ^1H NMR spectra. ^1H NMR spectra of products isolated from these reactions showed, in some cases a bewildering number of imine-derived resonances (no less than six such bands in some cases). Also consistent with the presence of several species in these preparations was the broad band at *ca.* 2.37 ppm arising from several different types of methyl protons (H_a in **I**). In all these preparations, however, a sharp resonance at 7.97 ppm was the strongest in the imine region and we now associate this with the hydroxo-derivative of LPd_2^+ which we shall refer to as hydroxo-LPd_2, the possible nature of which is discussed below. An orange-red crystalline solid showing a single imine resonance at 7.97 ppm in its ^1H NMR spectrum could be obtained from crude material showing a multiplicity of imine resonances, by recrystallisation from hot benzene or benzene-petrol, but recoveries from such recrystallisations were very variable, generally poor and occasionally negligible and it appeared that some sort of degradation accompanied the recrystallisation. A better procedure to obtain hydroxo-LPd_2 was to use an LPd_2- starting material which was very much more soluble in organic solvents than the hydroxo derivative so that the latter precipitated as it was formed; thus, the two-phase reaction between $LPd_2(C_2H_5CO_2)$ or, better, LPd_2 (iso-$C_3H_7CO_2$) in benzene–diethylether with aqueous tetrabutylammonium hydroxide gave a precipitate showing a single imine resonance at 7.97 ppm in its ^1H NMR spectrum.



V

Besides the imine-derived singlet at 7.97 ppm hydroxo-LPd_2 shows in its ^1H NMR spectrum a 2 proton signal at 7.31 ppm arising from the aromatic protons (H_c and $H_{c'}$ in **I**) somewhat broadened, as in other LPd_2 derivatives, and a 3 proton singlet at 2.36 ppm originating in the mythyl protons (H_a in **I**). Unfortunately signals associated with the OH group could not be detected, as is often the case with hydroxo complexes [7]. Only weak broad ν_{OH} absorption in the range 3200–3700 cm^{-1} could be observed in the IR spectrum. The molecular weight of hydroxo-LPd_2 in chloroform, determined by vapour pressure osmometry, was consistent with the formulation $[LPd_2(OH)]_n$ in which the average value of n increases with increasing concentration from *ca.* 3 to *ca.* 4 in the accessible concentration range. Cyclic structures in which hydroxide bridges between separate LPd_2^+ units rather than bridging within a unit, such as, for example, structure **VI** in the case where n = 3, appear very reasonable. It does not seem likely, on the basis of an examination of molecular models, bearing in mind structural features of the LPd_2 unit revealed by X-ray crystallography, that hydroxide would be able to bridge in a stable fashion within a single LPd_2^+ unit. X-ray crystallographic examination of six different LPd_2 derivatives [5, 8–10] indicates that the sulphur centre of L^{3-} generally adopts a basically tetrahedral arrangement, with



VI

a lone pair of electrons occupying one tetrahedral position; palladium–palladium distances vary from *ca.* 3.6 to *ca.* 4.0 Å and PdSPd angles from 110° to 123°. If a bridging hydroxide were to be introduced at normal Pd–O distances into an LPd_2^+ unit, it would have to adopt a position very close to the sulphur atom, perhaps unrealistically so, and also the O(H)–Pd–O(L) angle would be unusually large, unless the LPd_2^+ arrangement were considerably distorted from those indicated by the crystal structure determinations. Hydroxo–LPd_2 in $CDCl_3$ solution slowly degenerates at room temperature, the ^1H NMR spectrum slowly developing multiple imine resonances and becoming closely similar (but only after several days) to the spectra of the crude samples referred to above. For this reason the osmometric results must be viewed with some slight suspicion and consequently the formulation $LPd_2(OH,H_2O)$ with a hydrogen bonded bridging arrangement as in **V** cannot be entirely ruled out, although it is difficult to see how such decomposition, if it occurred to any significant extent during the osmometry, could lead to the observed high apparent molecular weight. The observed elemental composition is in excellent agreement with the formulation $[LPd_2(OH)]_n$ and agrees less well with the formulation $LPd_2(OH,H_2O)$ (see Experimental section) but the differences are too small to allow completely definite discrimination. It appears that the determination of the exact nature of hydroxo-LPd_2 must await an X-ray crystallographic study.

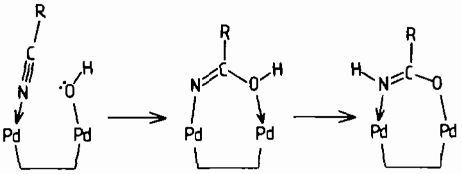
Media as weakly basic as aqueous carbonate-bicarbonate are sufficient to generate some hydroxo-LPd_2 from $LPd_2(CH_3CO_2)$; if a D_2O solution containing CO_3^{2-}, HCO_3^- and $N(C_4H_9)_4^+$ is stirred at room temperature with a solution in $CDCl_3$ of $LPd_2(CH_3CO_2)$, the gradual replacement of the features of $LPd_2(CH_3CO_2)$ in the ^1H NMR spectrum of the $CDCl_3$ layer by the features of hydroxo–LPd_2 can be observed. It seems that, under these conditions, the reaction ultimately reaches equilibrium in which significant $LPd_2(CH_3CO_2)$ remains, but after several hours secondary reactions as yet unidentified but presumably involving hydroxo-LPd_2, yield increasing quantities of by-products with imine resonances at 8.23, 7.95 and 7.81 ppm. The fact that considerable hydroxo–LPd_2 can be generated from $LPd_2(CH_3CO_2)$ and aqueous CO_3^{2-}/HCO_3^- suggests that a number of previously reported bridge substitutions upon $LPd_2(CH_3CO_2)$ conducted under two-phase $CHCl_3$ (or CH_2Cl_2)– aqueous CO_3^{2-} conditions, may have proceeded via hydroxo–LPd_2 [2–4].

When hydroxo–LPd_2 is dissolved in a mixture of equal parts of benzene and benzonitrile at room temperature a pale yellow crystalline solid starts to separate after only 5–10 min and the separation is complete after *ca.* 1 h. This product is identical to authentic $LPd_2(C_6H_5CONH)$ obtained by the bridge substitution reaction (under much more forcing conditions) between $LPd_2(CH_3CO_2)$ and benzamide [4].

A similar rapid reaction at room temperature occurs between acetonitrile and hydroxo–LPd_2 and this can be conveniently followed in solution by ^1H NMR spectroscopy. When CD_3CN is added to a solution of hydroxo–LPd_2 in $CDCl_3$, clean replacement of the features corresponding to the hydroxo derivative by those of $LPd_2(CD_3CONH)$ is observed. Authentic $LPd_2(CH_3CONH)$ can be prepared by the bridge substitution reaction between $LPd_2(CH_3CO_2)$ and acetamide in refluxing benzene–methanol and is characterised by the following spectroscopic features: IR, ν_{NH}, sharp but weak, 3360 cm^{-1}; amide derived bands at 1475 and 1560 cm^{-1}. ^1H NMR, pair of one proton singlets at 8.15 and 8.06 ppm arising from two inequivalent imine protons (H_f and $H_{f'}$ in **I**), a broad one proton signal at 5.62 ppm which disappears in the presence of D_2O arising from NH, a three proton singlet at 2.40 ppm corresponding to the methyl group (H_a in **I**) and a three proton singlet at 2.28 ppm arising from the methyl group of the CH_3CONH^- bridge. In the product generated from hydroxo–LPd_2 and CD_3CN (*i.e.* $LPd_2(CD_3CONH)$) the 2.28 ppm singlet is of course absent since the methyl group is deuterated. At 21 °C with a solvent mixture containing 15% by volume CD_3CN the reaction is *ca.* 50% complete after *ca.* 12 min and essentially complete after 1 h, as indicated by integration of the imine resonances. The reaction seems to be very clean. It is interesting that whereas resonances due to the OH of the hydroxo–LPd_2 cannot be observed in the ^1H NMR spectrum, these protons do become apparent in the NH of the product.

Using the acetate bridged complex as the promoter, acetonitrile could be hydrated to acetamide (bound as its conjugate base) under exceedingly mildly basic conditions at room temperature: thus, when a two-phase mixture consisting of $LPd_2(CH_3CO_2)$ in chloroform and an aqueous phase containing HCO_3^-, CO_3^{2-} and $N(C_4H_9)_4^+$ together with acetonitrile was stirred at room temperature for only 30 min, $LPd_2(CH_3CONH)$, identified by IR and ^1H NMR spectra, was isolated essentially quantitatively from the organic phase. This reaction could be conveniently followed, using a two-phase $CDCl_3/D_2O/CD_3CN$ mixture, by observing the ^1H NMR spectrum of the organic phase from time to time. In this way one could observe the progression from $LPd_2(CH_3CO_2)$ via intermediate mixtures containing significant amounts of deuteroxo-LPd_2, $LPd_2(CD_3COND)$ and unreacted $LPd_2(CH_3CO_2)$, ultimately to essentially 100% $LPd_2(CD_3COND)$ (See experimental section).

In view of ability of the LPd_2^+ unit to accommodate two separate ligands, it seems highly likely the above nitrile hydration reactions proceed via



VII

the 'non-bridged' intermediate **VII**, formed either by displacement of the water ligand by the nitrile, if hydroxo-LPd_2 has the formulation $LPd_2(OH,H_2O)$, or by breaking hydroxy bridges if the formulation is $[LPd_2(OH)]_n$. The base hydrolysis of nitriles normally proceeds at significant rates only under conditions very much more forcing than those described above and generally, further hydrolysis of the initial amide to give the corresponding carboxylate anion is more rapid than the first step, so the carboxylic acid is the normal product (after appropriate acidification) of such reactions. Bennett *et al.* have reported the hydration of nitriles to amides promoted by various mononuclear hydroxo–platinum(II) complexes [7], but these reactions are conducted at elevated temperatures (80 °C) and probably proceed by an entirely different mechanism, namely, these authors propose, attack of free OH^- on mononuclear, cationic platinum(II)–nitrile intermediates. Whilst we are unable to make quantitative comparisons and indeed such comparisons would probably be not very meaningful, it is clear that the crucial C–O bond forming step involves a much smaller energy barrier in our system. We propose that the organisation provided by L^{3-}, bringing the nucleophilic oxygen and the activated nitrile into appropriately close contact, is an important factor in the facility with which the C–O bond formation occurs. Obviously a number of species other than nitriles have the potential to play the role of X=Y in **II** → **III** and some of these possibilities with hydroxo–LPd_2 are presently being explored.

Experimental

$LPd_2(iso\text{-}C_3H_7CO_2)$

$LPd_2(CH_3CO_2)$ dissolved in isobutyric acid (10 cm^3 per g of $LPd_2(CH_3CO_2)$) was heated at 100 °C for *ca.* 5 min. The solution was evaporated to dryness under vacuum and the residue recrystallised from tetrahydrofuran-petroleum ether. Yield essentially quantitative.

Hydroxo–LPd_2

a) A solution of $LPd_2(CH_3CO_2)$ (0.20 g) in dioxan (6 cm^3 was stirred vigorously at room temperature with aqueous sodium hydroxide (1.5 cm^3, 0.5 M) for 8 h. The precipitated solid was separated by centrifuging and was washed with water (2 × 5 cm^3), dioxan (2 cm^3) and then diethylether (10 cm^3). The solid was dried in vacuum at 80 °C. Yield, 0.135 g. Recrystallisation from boiling benzene, with a hot filtration to remove some insoluble material, gave reddish-orange crystals, which were collected, washed with benzene and dried at 80 °C in vacuum. *Anal.* Found: C, 42.4; H, 4.7; N, 8.5: S, 5.0; Pd, 32.9. Calcd. for $C_{23}H_{30}N_4O_3SPd_2$ (*i.e.* $(LPd_2(OH))_n$): C, 42.3; H, 4.6; N, 8.5; S, 4.9: Pd, 32.5. Calcd. for $C_{23}H_{32}N_4O_4SPd_2$ (*i.e.* $LPd_2(OH,H_2O)$): C, 41.0; H, 4.8; N, 8.3; S, 4.7; Pd, 31.6.

b) A solution of $LPd_2(iso\text{-}C_3H_7CO_2)$ (0.12 g) in benzene (0.5 cm^3) and diethylether (2 cm^3) was vigorously stirred at room temperature with aqueous tetrabutylammonium hydroxide (0.35 cm^3, *ca.* 40%). Hydroxo–LPd_2 started to precipitate almost immediately and was collected after 80 min stirring. The solid was thoroughly washed alternately with water and ether and was dried in vacuum at room temperature. ^1H NMR and IR spectra were identical to those of the analytically pure material above.

Generation of Hydroxo–LPd_2 from $LPd_2(CH_3CO_2)$ and Aqueous Carbonate–Bicarbonate: ^1H NMR Study

To a stirred two-phase mixture of $LPd_2(CH_3CO_2)$ (0.053 g) in $CDCl_3$ (6 cm^3) and $D_2O/KHCO_3$ (3 cm^3, 2.2 M) was added tetrabutylammonium hydroxide in H_2O (*ca.* 0.02 cm^3, *ca.* 40%) (the hydroxide would be converted essentially to carbonate in the presence of excess bicarbonate). The mixture was stirred vigorously at room temperature and the organic phase examined by ^1H NMR spectroscopy from time to time. Integration of the imine signals gave an indication of the approximate relative amounts of $LPd_2(CH_3CO_2)$ and hydroxo–LPd_2 and (after prolonged reaction) other unidentified products. After 90 min $LPd_2(CH_3CO_2)$ and hydroxo–LPd_2 were present in roughly equal parts and a new unidentified LPd_2 derivative was just begining to be observable as a small resonance at 7.95 ppm. After 18 h the organic phase contained $LPd_2(CH_3CO_2)$ (*ca.* 25%), hydroxo LPd_2 (*ca.* 45%) and other unidentified products (*ca.* 30%) which gave new imine resonances at 8.23, 7.95 and 7.81 ppm.

$LPd_2(CH_3CONH)$ from Acetamide

A solution of acetamide (0.14 g) in methanol (2 cm^3) was added to a solution of $LPd_2(CH_3CO_2)$ (0.21 g) in boiling benzene (3 cm^3) and the resulting homogeneous solution was heated under reflux for 3 h. Boiling methanol (15 cm^3) was added to the hot reaction mixture and the resulting solution, upon cooling, gave a precipitate of $LPd_2(CH_3CONH)$ as fine yellow needles, which were collected, washed with methanol and dried in vacuum. Yield, 0.21 g.

Generation of $LPd_2(CH_3CONH)$ from $LPd_2(CH_3CO_2)$, Acetonitrile and Aqueous Carbonate–Bicarbonate

(a) Isolation of non-deuterated product

To a stirred two phase mixture consisting of $LPd_2(CH_3CO_2)$ (0.048 g) in chloroform (5 cm^3) and aqueous $KHCO_3$ (3 cm^3, 2.2 M) was added acetonitrile (0.2 cm^3) and aqueous tetrabutylammonium hydroxide (*ca.* 0.06 cm^3, *ca.* 40%) (the hydroxide would be converted essentially to carbonate in the presence of excess bicarbonate). The mixture was stirred vigorously at room temperature for 30 min. The organic phase was separated, washed with water and dried over Na_2SO_4 which was then removed by filtration. The filtrate, on evaporation under vacuum, gave a solid residue of $LPd_2(CH_3CONH)$, pure and uncontaminated by other LPd_2 derivatives on the basis of IR and ^1H NMR spectra, in essentially quantitative yield.

(b) ^1H NMR experiment

To a stirred two phase mixture of $LPd_2(CH_3CO_2)$ (0.051 g) in $CDCl_3$ (6 cm^3) containing CD_3CN (0.5 cm^3) and $D_2O/KHCO_3$ (3 cm^3, 2.2 M) was added tetrabutylammonium hydroxide in H_2O (*ca.* 0.02 cm^3, *ca.* 40%). The mixture was stirred vigorously at room temperature and the organic phase examined by ^1H NMR from time to time. Integration of the imine signals gave an indication of the approximate relative amounts of $LPd_2(CH_3CO_2)$, hydroxo–LPd_2 and $LPd_2(CD_3COND)$: after 37 min: $LPd_2(CD_3COND)$, (*ca.* 20%); hydroxo–LPd_2, (*ca.* 35%); $LPd_2CH_3CO_2)$ (*ca.* 50%). After 18 h: *ca.* 100% $LPd_2(CD_3COND)$ with no significant by-products.

Physical Measurements

IR spectra were recorded on a Jasco A 302 instrument either as KBr discs or nujol mulls. NMR spectra were recorded on a Jeol FX 100 spectrometer. Analyses were carried out by the Australian Microanalytical Service, Melbourne.

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